EFFECT OF A CATALYST ON THE DISSOLUTION OF BLIND CANYON COAL

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INTRODUCTION

The use of catalysts to improve the dissolution and liquefaction of coal dates back to the 1920s. Reviews in this area have been prepared by Weller (1), Derbyshire (2), and Anderson (3). Recently, interest has been renewed in using dispersed catalysts in the early phases of coal liquefaction to improve the quality of the products produced during the initial dissolution and liquefaction of coal. To facilitate the study of dispersed catalysts in laboratory-scale investigations, a particular sample of Blind Canyon coal (denoted DECS-17) that contains very low levels of pyrite (0.04 wt% on a moisture-free basis) has been made available by the Department of Energy through the Penn State Coal Sample Bank. Thus, complications due to inherent catalytic activity associated with pyrrhotites which can be formed from coal pyrite are eliminated and interferences to the characterization of the added catalysts due to native iron and sulfur are reduced.

The purpose of this paper is to define the effects of a molybdenum-containing catalyst on the initial dissolution and conversion of the DECS-17 coal as a function of temperature. To eliminate competing and/or complicating influences of added solvents, the liquefaction tests were performed in the absence of such materials. The catalytic effects on coal conversion and gas uptake were determined by subtraction of thermal data from the corresponding catalytic results at a given temperature. The results provide a picture of the reactivity of the DECS-17 coal and its response to a dispersed liquefaction catalyst.

EXPERIMENTAL

All of the experiments were performed with the DECS-17 Blind Canyon coal from the Penn State Coal Sample Bank. The coal was minus-60 mesh and was riffled prior to use. The elemental analysis (on a dry basis) provided with the coal was as follows: 76.3% carbon, 5.8% hydrogen, 1.3% nitrogen, 0.4% sulfur, 6.6% ash, and 9.7% oxygen (by difference). The moisture content of the as-received coal was 3.7%.

The liquefaction tests were conducted in 316 stainless-steel microautoclaves. The total internal volume, including connecting tubing, of the microautoclave used in most of this work was 49.0 cm³. During the tests, the microautoclave was mounted in a horizontal position and shaken in an arc motion at approximately 360 cycles per minute in a heated, fluidized sand bath.

The microautoclave was charged with 3.3 g of coal and, if used, 0.008 g of molybdenum hexacarbonyl, $Mo(CO)_6$. The $Mo(CO)_6$ was used as received from Strem Chemical Company. Purity was given as 98 + % with moisture being the only major contaminant. No special procedures were used to mix the $Mo(CO)_6$ with the coal; the compound was simply added from a spatula directly to the microautoclave containing the coal sample.

In all of the tests, an initial charge of 1030 psig (7.20 MPa) hydrogen gas containing 3% hydrogen sulfide was added to the microautoclave after it had been pressure tested and purged with nitrogen.

A series of tests were performed of 60 minutes duration at 325°C, 350°C, 375°C, 400°C, and 425°C. A slow heat-up procedure was employed in which the microautoclave was heated along with the sandbath from room temperature to the desired reaction temperature. The longest heat-up time was approximately 60 minutes to reach the highest temperature of 425°C. The temperature was monitored by a thermocouple placed inside the microautoclave. The pressure was monitored by an electronic pressure transducer connected to the microautoclave by a section of 1/8 inch (3.2 mm) stainless-steel tubing. Time, temperature, and pressure were recorded at ten-second intervals by a PC-based data acquisition system.

At the end of the 60-minute reaction period, the microautoclave was rapidly cooled in water. The gaseous contents of the microautoclave were then measured by water displacement and a gas sample was taken. The microautoclave was then opened and the contents removed with tetrahydrofuran (THF). Sonication was used to facilitate cleaning of the microautoclave and dissolution of the products.

The reaction products were extracted with THF using pressure filtration. The THF conversion was calculated by determining the difference in the weight of the starting coal and the insoluble residue. Cyclohexane conversion was similarly determined by adding the THF-soluble material to cyclohexane and performing another pressure filtration to recover the cyclohexane-insoluble residue. The THF and cyclohexane residues were dried at 110°C under vacuum to constant weight. The conversions are reported on a dry, ash-free basis.

RESULTS AND DISCUSSION

To determine the effects of a catalyst in coal liquefaction, it is useful to perform the liquefaction tests without added solvents or vehicles. Previous work has shown that fundamental catalyst investigations tend to be confounded if any solvents are present (1,2). In particular, the use of reactive liquids such as tetralin was found to exert a leveling effect on the influence of the catalyst on the initial conversion of coal (4). Using only coal and hydrogen magnifies the effect of the added catalyst.

In most solvent-free liquefaction work, a benefit is noted for impregnating the catalyst precursor on the coal over adding it as a powder (1,2). This is usually evident by higher conversions for the impregnated samples. To make the liquefaction tests as simple as possible, it was desirable to utilize a catalyst precursor that required few, if any, special preparation procedures to produce an active catalyst during the liquefaction test. Compounds commonly used in coal liquefaction research such as ammonium heptamolybdate, ammonium tetrathiomolybdate, and molybdenum trisulfide only perform well when special procedures are employed either to disperse or impregnate them onto the coal or to introduce them as very small particles.

$Mo(CO)_6$ is not commonly used as a catalyst precursor in coal liquefaction research. While it has been shown to be an effective precursor (5,6), it is not practical for use on a larger scale. However, certain attributes of $Mo(CO)_6$ make it desirable for fundamental investigations into catalytic mechanisms relative to coal liquefaction. In particular, the

inherent volatility of $Mo(CO)_6$ permits it to form an active liquefaction catalyst (MoS_2) in the presence of sulfur with no special preparation, impregnation, or dispersion techniques (4,6). The reactions involved in the transformation of $Mo(CO)_6$ to MoS_2 appear to take place in the gas phase as the carbonyl sublimes and decomposes. Conversion of $Mo(CO)_6$ to MoS_2 has been observed to occur at temperatures as low as 100°C in the presence of hydrogen sulfide (7).

Figure 1 shows the effect on the conversion of the DECS-17 coal of simply adding $Mo(CO)_6$ powder along with coal to the microautoclave. These tests were performed at 425°C using a slow heatup to reaction temperature and an initial charge of 1030 psig (7.20 MPa) hydrogen/3% hydrogen sulfide. Duplicate tests were performed with the raw coal (indicated in Figure 1 at 10 ppm) and with 100 ppm added molybdenum. Six replicate tests were performed at a level of 1000 ppm added molybdenum. The bars associated with the data points in Figure 1 indicate the range of values obtained (the results were identical for the tests with raw coal). Good conversions to both THF and cyclohexane-soluble products are noted at catalyst concentrations of 500 ppm Mo (based on daf coal) or above. These conversions are similar to those obtained with this coal when using a hydrogen-donor solvent in conjunction with more conventional catalyst precursors (8). A pronounced catalytic effect is noted even at molybdenum loadings of 50 to 100 ppm. There does not appear to be much additional benefit of using catalyst loadings above 1000 ppm.

To determine the effect of $Mo(CO)_6$ on the conversion of DECS-17 coal as a function of temperature, liquefaction tests were performed at 25°C intervals from 325°C to 425°C in the presence and absence of this compound. In the catalytic tests, $Mo(CO)_6$ was used at a level of 1000 ppm Mo (based on daf coal). Table I summarizes the number of replicate experiments that were performed in each case.

Table I. Number of Duplicate Tests Performed on the DECS-17 Coal.

Reaction Temperature, °C	Number of Tests Performed	
	Thermal Tests	Catalytic Tests
325	2	2
350	4	4
375	3	2
400	4	2
425	4	6

The conversion data for the thermal and catalytic tests are shown in Figures 2A and 2B, respectively. The symbols represent the average conversion value and the bars associated with the symbols indicate the range of values obtained. No bars imply that the variability was less than two percentage points of conversion (the size of the symbols). The figures reveal that greater variability in conversion values was associated with specific conditions. For example, the greatest variabilities were associated with determinations of cyclohexane conversion for the catalytic tests. It was also noted that

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the filtration of the THF solution from the catalytic test at 375°C was much more difficult than for the same product at the other temperatures, resulting in greater variability than for the same determination at the other temperatures.

It is evident from the data in Figure 2B that high conversions of the DECS-17 coal are possible with $Mo(CO)_6$ in the absence of any added solvents or vehicles. The THF and cyclohexane conversions at 425°C are over 90% and 60%, respectively. Similar conversions were previously obtained using $Mo(CO)_6$ with an Illinois No. 6 coal (6). Both the thermal and catalytic conversions increase with temperature; however, the influence of the catalyst becomes more apparent at higher temperature.

To better illustrate the effect of the catalyst, Figure 3 contains the differences obtained by subtracting the thermal conversions from the corresponding catalytic conversions. Little or no catalytic effect is observed at 325°C. Other data, which are not presented here, show that a catalytic effect is observed at this temperature at longer reaction times. As the reaction temperature increases, there is a corresponding increase in the additional amount of THF conversion due to the effect of the catalyst. The catalytic effect levels as the maximum total conversion is approached (400°C). The greatest increment to the catalytic effect on THF conversion occurs between 350°C to 375°C.

A different trend is observed for cyclohexane conversion. In this case, no activity is observed until the reaction temperature exceeds 375°C, at which point the conversion attributed to the catalyst suddenly increases. In going to 425°C, a smaller increase is noted. Figure 2A shows that the thermal conversion to cyclohexane-soluble materials increases steadily from 325°C to 425°C.

Based on the above data and observations of the resulting products, it appears that the catalyst formed from $Mo(CO)_6$ plays two separate roles in the liquefaction of the DECS-17 coal. First, it facilitates the dissolution of the coal to heavy products in a manner that parallels increases in reaction temperature. Second, it improves the conversion of these products to lighter, cyclohexane-soluble material. The onset of catalytic activity occurs at a higher temperature for the latter role. At present, it is not clear whether the difference in onset temperatures for the two catalytic functions is due to differences in activation energies for the catalytic reactions responsible for these two roles, or whether the catalyst itself changes in activity as the reaction temperature is increased. Further experiments would be required to differentiate between these effects. One possibility is that the two roles may be explained on the basis of two different chemical functions. That is, THF conversion is catalytically assisted by prevention of retrogressive reactions while cyclohexane conversion is assisted by catalysis of cracking or deoxygenation reactions.

The conversions noted above are calculated by difference using the weights of the insoluble residues collected and thus do not differentiate between the yields of liquid and gaseous products. Figure 4 shows the average production of gaseous products for the thermal and catalytic tests at the various temperatures. It is apparent that most of the gases produced are the result of thermal chemistry. The largest increase in gas production occurs between 400°C and 425°C. Only the production of butane and, to a lesser degree, propane are influenced by the presence of the catalyst. The increased production of these species again points to increased cracking activity, possibly of hydroaromatic ring structures.

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Analysis of the quantity and composition of the gas released when the microautoclave was depressurized permitted calculation of the amount of hydrogen consumed during the reactions. Figure 5 compares the increment in conversion with the increment in hydrogen uptake resulting from the addition of the catalyst. The trends are similar to those in Figure 3 and are consistent with two separate roles of the catalyst. The catalytic promotion of hydrogen uptake is associated with a regular corresponding increase in THF conversion. This is not the case for cyclohexane conversion. This indicates that catalytically promoted hydrogen uptake is insufficient in and of itself to produce lighter or less functional liquefaction products. Catalytic influence on cracking or deoxygenation reactions may require higher temperatures.

The total pressure within the microautoclave was also recorded over time for each test. These data were converted to estimates of the moles of gas in the microautoclave using the ideal gas law and an experimentally derived correlation between measured pressure and reactor temperature. Figure 6 depicts the effect of the catalyst on the rate at which the amount of gas present in the microautoclave changed during the liquefaction tests at the different temperatures. The decreases noted in this figure are primarily due to the uptake of hydrogen. The results are averages of at least two sets of experiments and again are determined by subtracting the thermal data from corresponding catalytic data. The abscissa, time, includes the heat-up period and the one hour reaction time. Little influence of the catalyst on the rate of hydrogen uptake is noted at 325°C. A slightly higher rate is observed at 350°C; however, at even higher temperatures a pronounced increase in the rate of hydrogen uptake is noted. The onset of this pronounced catalytic activity occurs at about 370°C. It also appears that a limit for the catalytic influence on hydrogen uptake of about 0.016 moles is approached at 425°C. This is equivalent to 0.011 grams of hydrogen per gram of coal.

SUMMARY

The preliminary work presented here with the DECS-17 Blind Canyon coal shows the importance of utilizing a catalyst in the dissolution and liquefaction of this coal. Under the conditions of the tests reported here, the catalyst appears to have dual roles in the conversion to THF- and cyclohexane-soluble products. The catalyst appears to be active at 350°C with respect to formation of the THF-soluble products; however, no activity is observed with respect to cyclohexane-soluble products until 400°C.

Overall, the data show that high conversions of this coal are possible using only a dispersed catalyst (no added solvents) and hydrogen. In particular, operation at 400°C results in high conversion but with much lower gas production than at 425°C. If one is going to study the effect of a catalyst on the initial dissolution of this coal, it would be advisable to operate at temperatures below 400°C. If interest is in the production of lighter products, then 400°C or higher should be used.

ACKNOWLEDGMENTS

DISCLAIMER

Reference in this report to any specific product, process, or service is to facilitate understanding and does not imply its endorsement or favoring by the United States Department of Energy.

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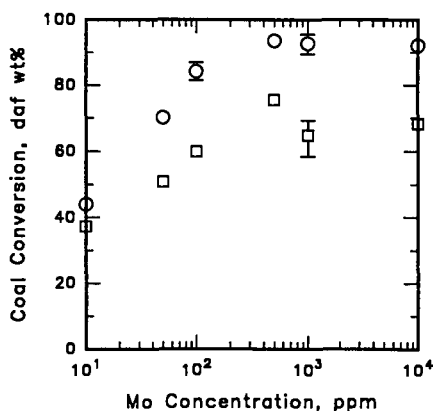
Figure 1. Effect of adding $Mo(CO)_8$ on the conversion of DECS—17 coal. (O THF solubility; □ cyclohexane solubility. Data at 10 ppm are for raw coal.)
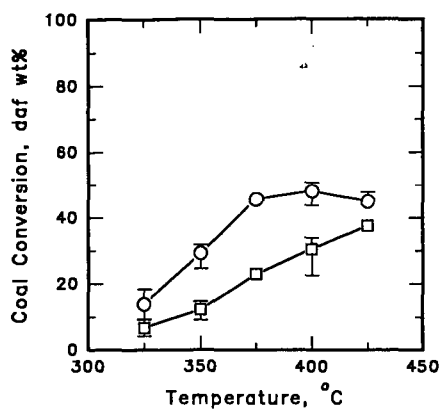
Figure 2A. Conversion results from thermal
liquefaction tests. (O THF solubility;
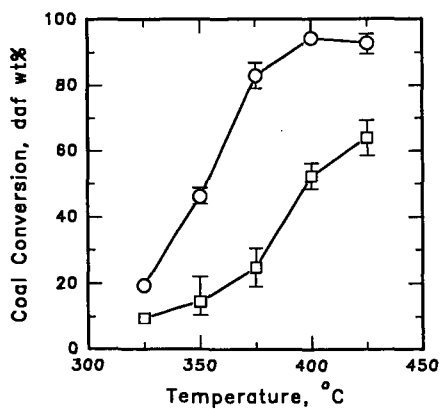☐ cyclohexane solubility)

Figure 2B. Conversion results from catalytic
liquefaction tests. (O THF solubility;
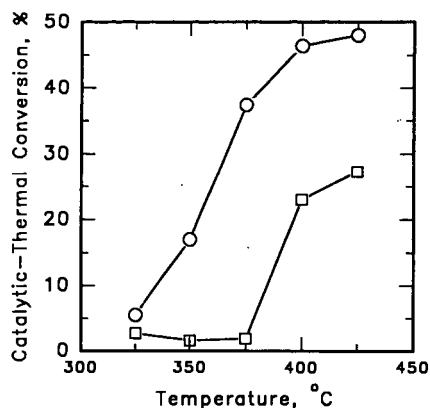☐ cyclohexane solubility)

Figure 3. Catalytic–thermal conversions.
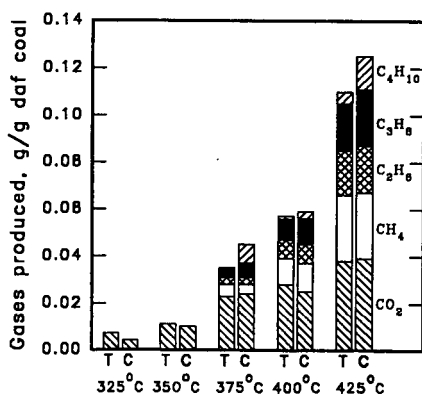(O THF solubility; □ cyclohexane solubility)

Figure 4. Average gas production for DECS–17 coal for thermal (T) and catalytic (C) tests at different temperatures (shown on abscissa).
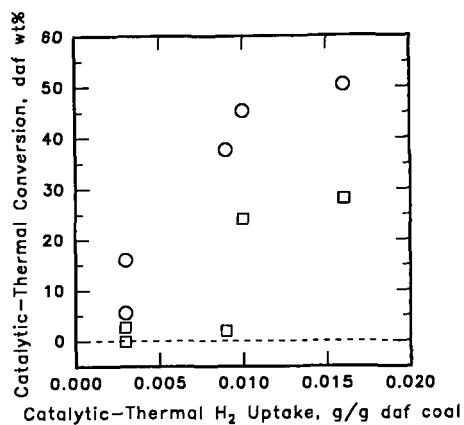
Figure 5. The effect of a catalyst on conversion
as a function of the effect of a catalyst on
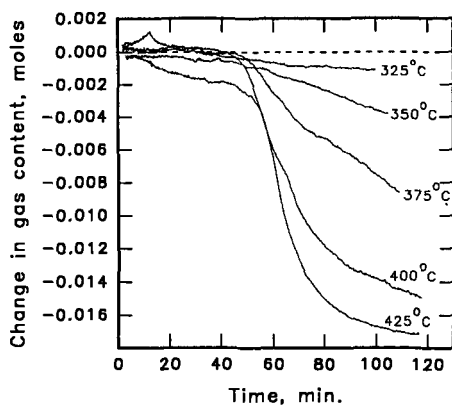hydrogen uptake. (○ — THF solubility; □ —
cyclohexane solubility)

Figure 6. Effect of a catalyst on changes
in gas content as a function of time and
temperature. Trends are averages of
catalytic—thermal data.